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Coupling UF and micro-waves to accelerate ageing of PES membrane by sodium hypochlorite: A lab scale methodology allowing preparation of aged membrane similar to long term aged membrane obtained at industrial scale

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In dairy industry, ageing of polyethersulfone (PES) ultrafiltration membranes is mainly related to degradation provoked by NaOCl used for disinfection (150-200 ppm NaOCl at pH 11.0-11.5, 50°C) [1, 2]. At industrial scale, production disruptions due to the membrane ageing are not easy to predict. Consequently membranes are often changed in emergency conditions due to severe failures. A real need of fundamental studies exists: firstly to understand the fundamental origins of the membrane ageing and secondly to propose tools for evidencing progressive degradation allowing prevention. An important limitation for such studies is the ability to obtain degraded membranes, the ageing state of which is representative of industrial ageing state. Moreover the protocol must be short time consuming to be compatible with an efficient research. With the objective of reducing the duration of lab experiments, already proposed procedures consist generally in static immersion of membranes in NaOCl solutions much more concentrated than that used at industrial scale [3]. Such protocols allow obtaining chemically aged membranes, the representativity of which is not established. For many years now, we try to establish such a suitable protocol for PES membranes used for skim milk UF. It must be underlined that PES membranes used in water treatment suffer from the same ageing phenomenon. Thus the proposed methodology could probably be transposable to other applications fields than food industry.

As pre-requisite, the methodology must establish a comparison between a virgin membrane and an industrial membrane at end of its service-life, and it must be able to distinguish intermediate degradation states. The degradation can be evidenced according to two complementary sets of characterisations: from a physico-chemical point of view (variation in composition and of physico-chemical characteristics) and from the process point of view (behaviour during UF). The physico-chemical characterisations successfully used in the present study are FTIR-ATR, SEM-EDX, SIMS, contact angles, streaming potential.... The membrane behaviour in UF conditions is followed with ageing state (water permeability, retention of a model protein, namely lysozyme 14 $kg.mol^{-1}$). Ideally, correlations between the two sets of experiments could be proposed. The chosen PES membrane (HFK-131, MWCO: 5-10 $kg.mol^{-1}$, Koch) is widely used all around the world. In fact this membrane contains some nitrogen (SIMS) and not only C, S, O as drawn from PES formula. Knowing that polyvinylpyrolidone (PVP) is often used as additives during membrane preparation we have supposed that N could come from PVP. To re-enforce this hypothesis model films made of PES+PVP (95/5) were prepared. FTIR-ATR spectra of model films and membranes (Figure 1) match well. PVP occurrence in membrane is evidenced as by a band located at 1660 cm^{-1}. An industrial membrane at end of life (8,000 h in skim milk UF conditions) has been carefully analysed [2]. FTIR-ATR analyses reveal that in addition to residual proteins, identified as long term irreversible fouling, some new bands appeared on spectra, located at 1030 cm^{-1} and 1720 cm^{-1} whereas the band at 1660 cm^{-1} has disappeared. Moreover the membrane permeability to water was highly increased (not similar all over the membrane and estimated to be up to 4-5 times that of a virgin membrane – autopsy of two virgin spiral membrane performed in parallel evidences also significant permeability gradient).

For ageing experiments, the composition of the NaOCl solution must be first chosen. Concentration was selected from ageing states reached by static immersion of PES flat membranes at 50°C followed over year (in the range 0 to 96,000 ppm in total chlorine at pH 8.0 and 11.5). Accordingly concentration of NaOCl might be 400 ppm maximum as more concentrated solutions led to too highly damaged membranes. Generally speaking, for a given

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concentration, damaged provoked by solutions at pH 8.0 are similar to those obtained at pH 11.5, except the kinetic; the lower the pH is the quicker the ageing is. The 400 ppm NaOCl solution at pH 8.0 appears as a good candidate as only 3 bands located at 1660, 1030 and 1720 cm^{-1} varied on FTIR-ATR spectra in good agreement with the industrially aged membrane.

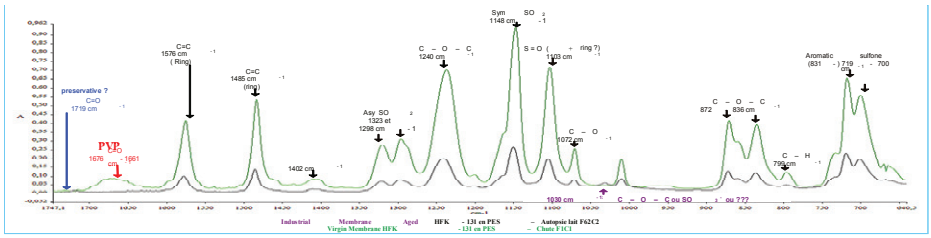

***Figure 1**. FTIR-ATR spectra of pristine (green) and industrially aged membrane (black)*

With the selected NaOCl solution, 3 protocols (at 50°C) were tested at 50°C with the aim of first reaching the physico-chemical target ageing state: (i) long time static immersion (up to a year) – (ii) short time immersion (from few minutes up to few hours) under micro-waves (60 W (continous) – 170 W (pulsed) – 650-680 W (pulsed)) – (iii) middle time (up to a week) immersion in UF conditions at 2 bar. From variation of both 1030 and 1660 cm^{-1} band of FTIR-ATR spectra and other physico-chemical analyses the following equivalence can be suggested: 4,000-8,000 ppm.day in static immersion ≈ 18,000 ppm.min with pulsed micro-waves (650-680 W) ≈ 96,000 ppm.min with continuous micro-waves (60 W) ≈ 500 - 1,300 ppm.day in UF. Comparisons allow also drawing that both chemical ageing and mechanical ageing are superimposed to lead to the target ageing state. Then a cascade of short UF ageing (30 h = 500 ppm.day) + short time micro-waves 1 h - 20 h ((170 W) was tested. Figure 2 evidences good obtained results. Retention of model protein was also in good agreement (not shown). Finally the cascade is validated as lab scale ageing and is now applied with the aim of an online evidencing of ageing through the retention behaviour of several target molecules naturally existing in skim milk

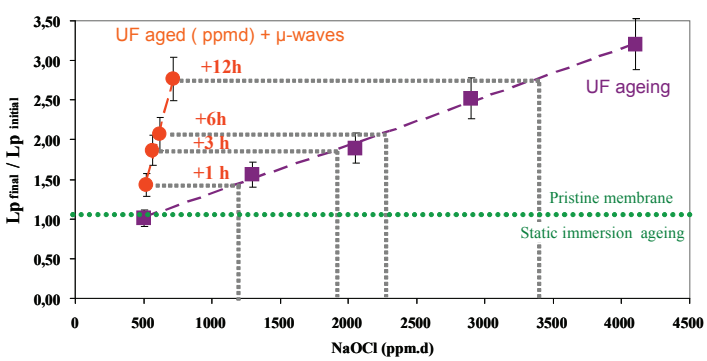

Figure 2: Summary of the variation of membrane permeability Lp final (compared to Lp initial corresponding to the pristine membrane) versus ageing protocol

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References

1. L. Bégoin, M. Rabiller-Baudry, B. Chaufer, M.C. Hautbois, T. Doneva, Desalination 192 (2006) 25–39

2. L. Bégoin, M. Rabiller-Baudry, B. Chaufer, C. Faille, P. Blanpain-Avet, T. Bénézech, T. Doneva, Desalination 192 (2006) 40–53

3. S. Rouaix., C. Causserand, P. Aimar, J. Membrane Sci. 277 (2006) 137-147.

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